

Nanographene Favors Interactions with the Electron Acceptor Rather Than the Electron Donor in a Planar Fused Push-Pull Conjugate

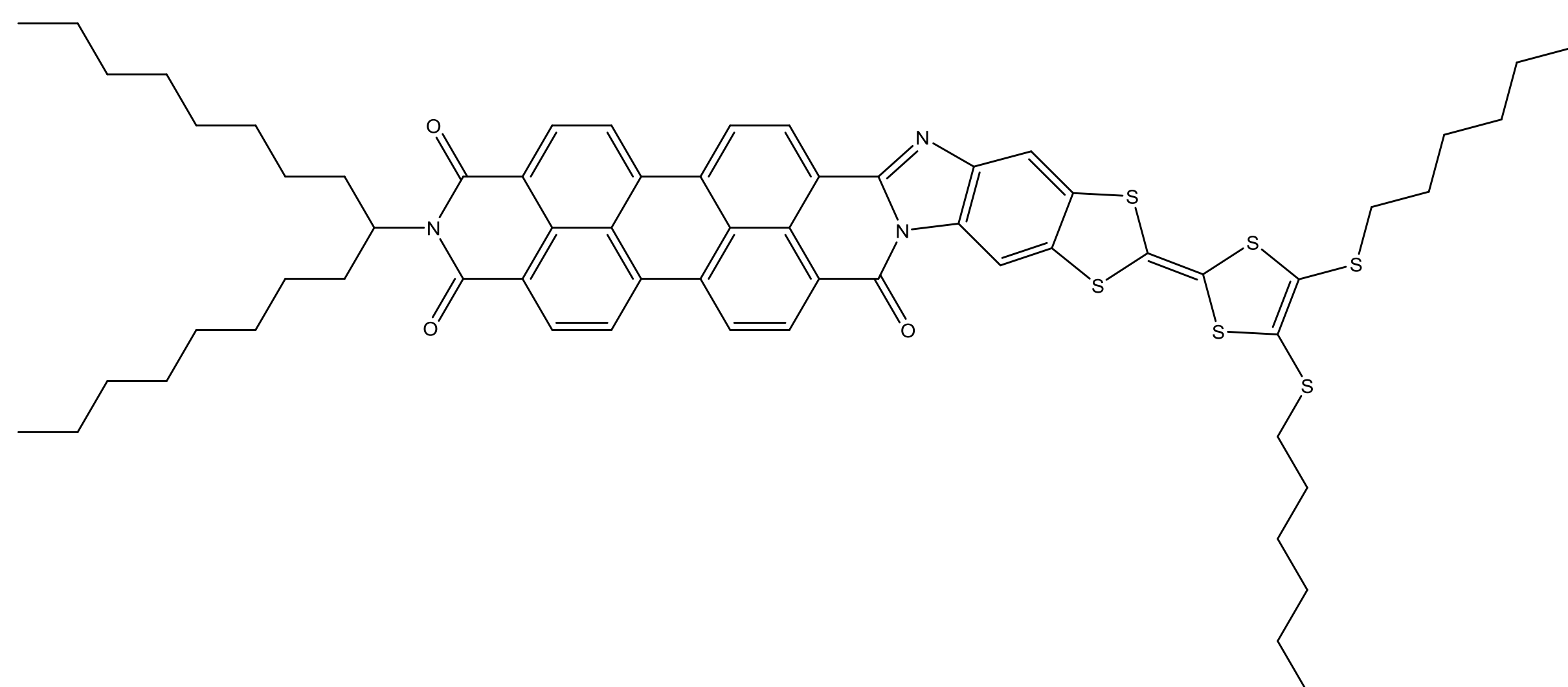
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Abstract: Dispersions of preexfoliated nanographene (NG) and fused electron donor–acceptor tetrathiafulvalene–perylene-3,4,9,10-tetracarboxylic diimide (TTF–PDI) enable multifunctional, noncovalently functionalized NG. They were characterized by complementary spectroscopic and microscopic techniques. The design strategy of the chromophoric and electroactive molecular conjugate renders a large and planar π -extended system with a distinct localization of electron-rich and electron-poor parts at either end of the molecular conjugate. Within the in-situ formed nanohybrid, the conjugate was found to couple electronically with NG preferentially through the electron accepting PDI rather than the electron donating TTF and to lead to p-doping of graphene.

Introduction: Molecular films of graphene have the potential for the much needed breakthroughs in nanoelectronic devices.^[1] Non-covalent functionalization of graphene does not disrupt the extended π -conjugation. Incorporation of intercalators in the form of redox- and/or photoactive building blocks enables the usage of electron donor-acceptor (D–A) interactions. Accordingly, the non-covalent functionalization of nanographene (NG) or graphene sheets with either aromatic electron donors or acceptors, as demonstrated in the case of carbon nanotubes, is widely exploited in contemporary research.^[2] Herein, we report the exfoliation of graphite through intercalation and immobilization of a planar and extended π -conjugated D–A **1** (Scheme 1) onto its basal plane and the resultant nanohybrids have been characterized by complementary spectroscopic and microscopic techniques.^[3]



Scheme 1 Chemical structure of the TTF-fused PDI **1**.

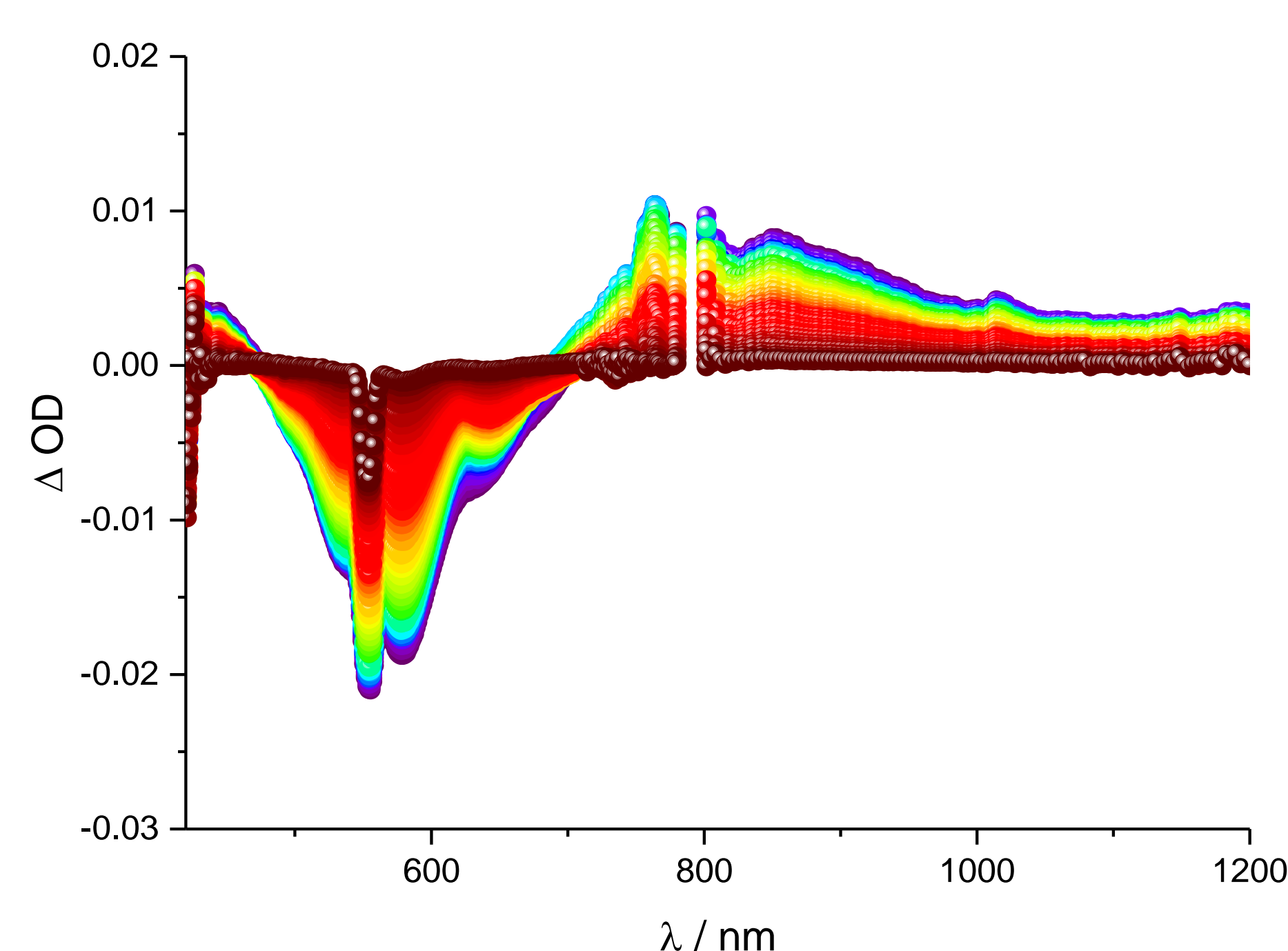


Figure 1. Differential absorption spectra (Vis and NIR) obtained upon femtosecond pump probe experiments (550 nm) of **TTF-PDI** in THF with time delays between 2.1 (blue) and 7500 ps (red).

Figure 1 shows that the differential absorption characteristics of the PDI-centred singlet excited state emerge in the form of minima in the 535 to 570 nm range after excitation. Furthermore, features in the 700 to 900 nm range are assigned to singlet-singlet transitions, as well as to the fingerprint of the one-electron reduced form of PDI resulting from an intramolecular charge transfer (ICT). Independent confirmation for the intramolecular ICT nature stems from transient absorption measurements with a 530 nm excitation wavelength, where monomers are likely to absorb. Here, the markers of the one-electron reduced form of PDI at 735 and 825 nm are clearly distinguishable from the broad singlet-singlet transitions.

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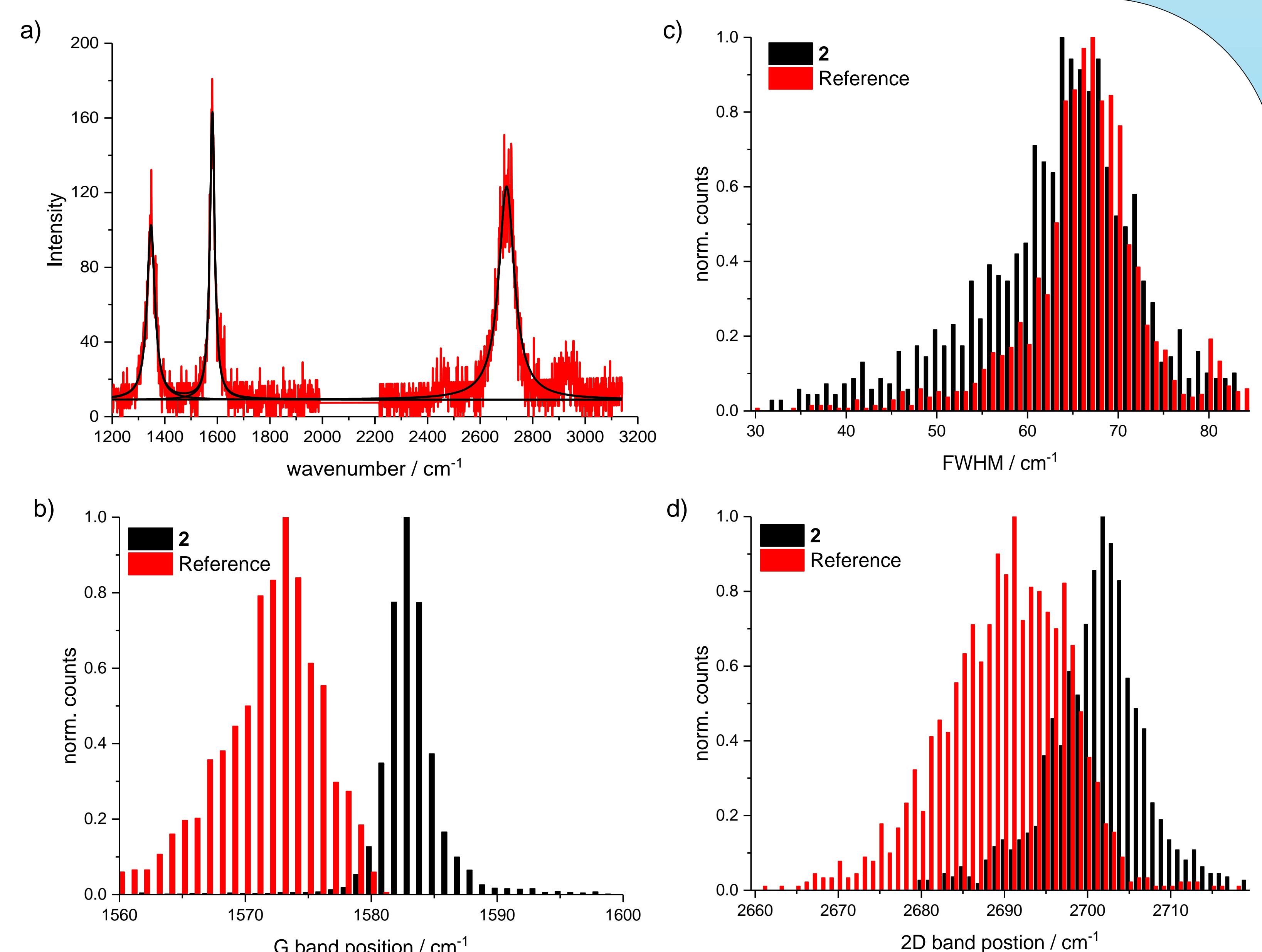


Figure 2. a) Selected Raman spectrum of **nanohybrid 2**. b) Histogram of 2D band FWHM of **2** and a **reference dispersion (R)**. c) Histogram of the G band position of **2** and **R**. d) Histogram of the 2D band position of **2** and **R**.

Figure 2 shows a selected Raman spectrum of nanohybrid **2** formed by immobilization of **1** onto the preexfoliated nanographene, and the statistical data regarding the FWHM of the 2D band as well as the positions of the G- and the 2D-bands. FWHMs for both dispersions peak at the same value, namely 65 cm^{-1} , suggesting the presence of turbostratic graphite. By monitoring and comparing the position of the G- and the 2D-bands of nanohybrid **2** with a reference dispersion (**R**), a clear upshift is observed. This is due to the electron accepting nature of PDI and suggests p-doping of the graphene sheets.

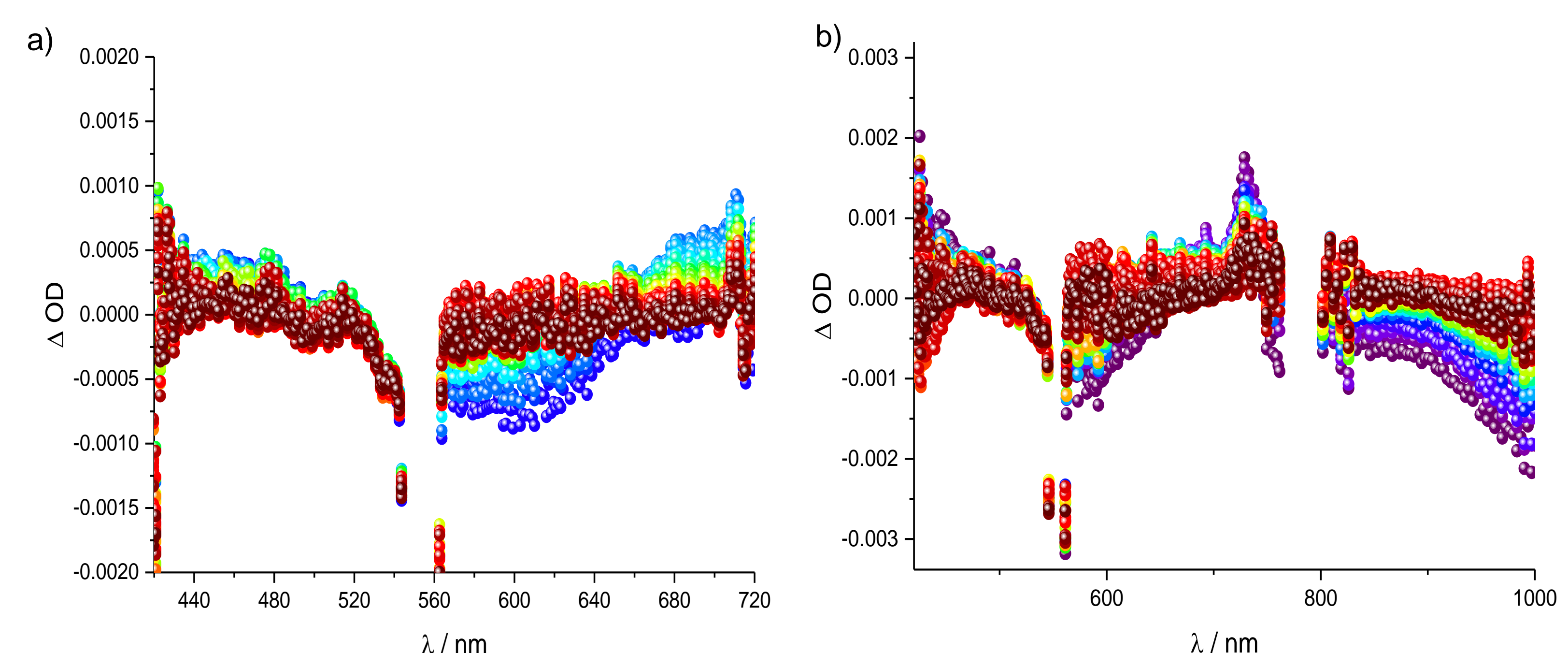


Figure 3. a) Differential absorption spectra obtained upon femtosecond pump probe experiments (550 nm) of nanohybrid **2** in THF with time delays between 1.3 (blue) and 20 ps (red). b) Differential absorption spectra obtained upon femtosecond pump probe experiments (550 nm) of nanohybrid **2** in THF with improved white light settings with time delays between 2.2 (blue) and 9 ps (red).

These comprise PDI related ground-state bleaching in the region of 500 – 600 nm as well as graphene related bleaching in the NIR region. Importantly, the new transient between 700 and 850 nm is attributed to the one-electron reduced form of PDI due to electron transfer from graphene to PDI.

Conclusion: A planar and fused TTF-PDI push-pull **1** was synthesised to exfoliate graphite *via* intercalation and immobilization onto its basal plane. Within the in-situ formed nanohybrid, the ground state CT from the graphene to PDI is the inception to a full charge separation in the excited state to afford the one-electron reduced form of PDI.